metal-organic compounds

A monoclinic pseudopolymorph of manganese squarate dihydrate, Mn(μ-C$_4$O$_4$)(H$_2$O)$_2$, built from cubic units

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The structure of poly[[[hexaaquatrimanganese(II)]-tri-μ-squarato] monohydrate], $\{[Mn_3(C_4O_4)_3(H_2O)_6]\cdot H_2O\}_n$, synthesized hydrothermally, consists of a new three-dimensional framework described by secondary building units (SBUs) containing two MnO$_6$ octahedra and three squarate groups in a cube-shaped arrangement. In the asymmetric unit, one squarate group is located around an inversion centre (4a; 0, 0, 0), two Mn atoms [4d ($\frac{3}{4}$, $\frac{1}{4}$, 0) and 4c ($\frac{1}{4}$, $\frac{1}{4}$, 0)] are located on inversion centres and the third Mn atom is on a twofold axis (4e; 0, y, $\frac{1}{4}$). This report illustrates the concept of the SBU and the flexibility of the squarate spacer in the design of new porous topologies.

Comment

The design and construction of metal–organic frameworks (MOFs), based on the concepts of building units, scale chemistry and interconnected networks [see, for example, Férey (2000) and O'Keeffe *et al.* (2000)], have attracted increasing interest in recent years owing to the versatility of the new topologies that can be prepared. MOFs possess numerous applications, including selective sorption and separation, ion exchange, catalysis, gas detection and molecule storage (Férey *et al.*, 2005; Roswell & Yaghi, 2005, and references therein; Pan *et al.*, 2006). Multidentate organic ligands have been widely used to create new architectures. Efforts have focused mainly on carboxylates, whereas oxocarbon dianions have been less thoroughly investigated. Nevertheless, in association with transition metals, 3,4-dihydroxy-3-cyclobutene-1,2-dione (C$_4$H$_2$O$_4$), also known as squaric acid, allows the design of new topologies composed of chains (Lee *et al.*, 1996; Alleyne *et al.*, 1998), layers (Lee *et al.*, 1996; Lin & Lii, 1997; Näther *et al.*, 2002) and three-dimensional frameworks (Lee *et al.*, 1996; Lin & Lii, 1997; Neeraj *et al.*, 2002; Greve & Näther, 2002). The last case is rarely encountered, because stacking of the square anions frequently occurs. Furthermore,

the squarate dianion can act as a terminal, chelating or μ to μ_6 bridging ligand, offering a wide range of possible new designs.

In this context, detailed structural information is required in order to understand the properties of MOFs. The present study describes the crystal structure of the title compound, (I), a new three-dimensional open-framework manganese squarate. The compound was initially identified from powder X-ray diffraction, and pattern indexing suggested that it was new. It was subsequently verified that the powder pattern was in agreement with the pattern calculated from the single-crystal structure determination. The crystal structure of (I) (Fig. 1) is built from MnO$_6$ octahedra connected through squarate oxoanions. Each polyhedron is surrounded by 12 octahedra *via* four oxoanions, and each squarate anion is connected to four metal atoms. This arrangement generates a three-dimensional metal–squarate framework. It can be described by cube-shaped secondary building units (SBUs) connected to one another through common faces (Fig. 2). Each unit comprises Mn1O$_6$ and Mn2O$_6$ octahedra, which are located alternately at the vertices of the unit; the squarate groups SQ1 [C1–C4/O1/O2^{vi}/O3/O4; symmetry code: (vi) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$] and SQ2 [C5/C6/O5/O6/C5^{vii}/C6^{vii}/O5^{vii}/O6^{vii}; symmetry code: (vii) $-x, -y, -z$], located at the centre of each edge along the c axis and the a and b axes, respectively; and an Mn3O$_6$ octahedron, which is located at the centre of the SBU.

(I)
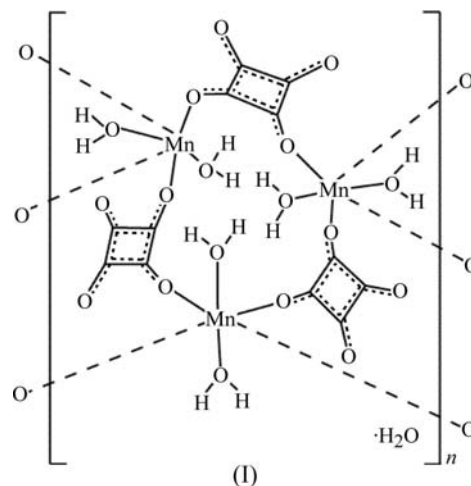
Each unit, with dimensions $a \times b \times c/2$, contains two octahedra (four Mn1O$_6$ and four Mn2O$_6$ located on the corners of the cubic SBU, and one Mn3O$_6$ at the centre of the SBU) and three squarate groups (four SQ1 and eight SQ2 located on the edges of the cubic SBU). There are no interactions between neighbouring squarate groups, since the stacking distance between square centroids is too high (Hunter & Sander, 1990; Tsuzuki *et al.*, 2002). Solvent-accessible voids were calculated by means of the programs SQUEEZE/SOLV included in *PLATON* (Spek, 2009). The total volume available for guest molecules is 448 Å^3, distributed over four cavities, which corresponds to approximately 20% of the total unit-cell volume. The total electron count per unit cell is 45, *i.e.* 10 electrons per void, which means that one water molecule (11 e) could be accommodated in each void. The largest residual peak (1.31 e Å^{-3}) in the final refinement

is located in the void at $(0, -0.007, \frac{3}{4})$. Attempts to include a water molecule in the model have been made. The largest residual peak dropped to 0.84 e Å^{-3}, with comparable reliability factors. Unfortunately, the atomic displacement parameters could not be refined satisfactorily and diverged to large values, and therefore no additional water molecule has been included in the model. If SQUEEZE data are used for the refinement, the largest residual peak drops to 0.48 e Å^{-3} and the R factor drops to 0.035.

There are 12 Mn atoms in the unit cell, lying on three crystallographically independent special positions, *viz.* Mn1 (4*d*) and Mn2 (4*c*) on an inversion centre, and Mn3 (4*e*) on a twofold axis. Each Mn atom is surrounded by two water molecules and four O atoms belonging to four different squarate groups. Each polygon is a near regular octahedron, with the four atoms of the square base strictly in the same plane for Mn1O$_6$ and Mn2O$_6$ and nearly planar for Mn3O$_6$ (the mean-square deviation is 0.0229 Å). The two atoms in apical positions (two water molecules) are equidistant from the mean plane and lie at the shortest Mn—O distances (Table 1). The mean Mn—O distance [2.17 (2) Å in the three octahedra; Table 1] is in agreement with the value of 2.197 Å calculated by the bond-valence method (Brown, 1996) and with the mean distances reported by Alleyne *et al.* (1998), Näther *et al.* (2002), Greve & Näther (2002) and Neeraj *et al.* (2002) for six-coordinated Mn atoms in squarate compounds. There are 12 squarate anions in the unit cell, lying on two sets of crystallographically independent general positions. Both oxoanions have the same μ_4 tetra-monodentate connection

mode (η^1:η^1:η^1:η^1; Fig. 1 and Table 1). The mean distances [C—C = 1.462 (2)/1.464 (2) Å and C—O = 1.252 (1)/ 1.253 (3) Å for SQ1/SQ2] and angles [C—C—C = 90.0 (1)° for SQ1 and SQ2] within the squarate groups are close to the values reported by West (1980). Moreover, the SQ2 group is strictly planar because it is located across a centre of inversion, and SQ1 is nearly planar, with a mean atomic deviation from the least-squares plane of 0.0197 Å.

Furthermore, the structure is reinforced by a three-dimensional network of hydrogen bonds [$D \cdots A$ = 2.7505 (18)– 2.7873 (18) Å; Table 2] between the coordinated water molecules, as H-atom donors, and O atoms belonging to the squarate anions, as acceptors.

Three other manganese squarates have already been reported, namely Mn(μ_2-C$_4$O$_4$)(H$_2$O)$_4$ (Weiss *et al.*, 1986), which crystallizes in the monoclinic system [space group Cc, a = 9.054 (8) Å, b = 13.506 (11) Å, c = 6.711 (6) Å, β = 95.41°] and which is isotypic to the iron squarate analogue (Frankenbach *et al.*, 1992), Mn(μ_4-C$_4$O$_4$)(H$_2$O)$_2$ (Neeraj *et al.*, 2002), which crystallizes in the trigonal system [space group $R\overline{3}$, a = 11.607 (5) Å, c = 14.66 (3) Å; reduced rhombohedral unit cell: a = 8.294 Å, α = 88.88°], and Mn(μ_4-C$_4$O$_4$)(H$_2$O)$_2$·0.93H$_2$O (Greve & Näther, 2002), which crystallizes in the cubic system [space group $Pn\overline{3}n$, a = 16.5527 (8) Å (= reduced cell)]. The tetrahydrate squarate is made up of chains, and dehydration to the dihydrate squarate leads to a condensation of the crystal structure. The two other reported manganese squarates possess three-dimensional frameworks. The title compound is a pseudopolymorph of the trigonal dihydrate squarate and of the partially hydrated cubic squarate. These three squarates display closely related crystal structures. Indeed, the crystal structures of the trigonal and cubic manganese squarates can also be described in terms of similar cube-shaped SBUs composed of two MnO$_6$ octahedra and three squarate anions, and the reduced unit cell is related to that of the title compound (a = b = 8.287 Å, c = 16.567 Å, α = β = 90.06° and γ = 91.25°). The three reduced unit cells are approximately orthogonal, and their volumes are twice, four times and 16 times that of the SBU (~285 Å^3) for the trigonal squarate, the
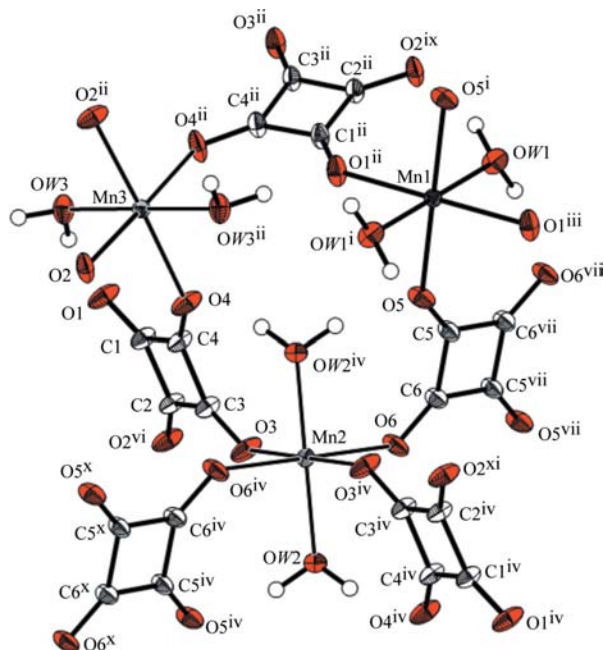

Figure 1
A view of the crystal structure of the title compound, showing the Mn coordination and the tetra-monodentate connection mode of the squarate anions. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $-x, y, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x, -y, -z$; (ix) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (x) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (xi) $x, -y, z - \frac{1}{2}$.]
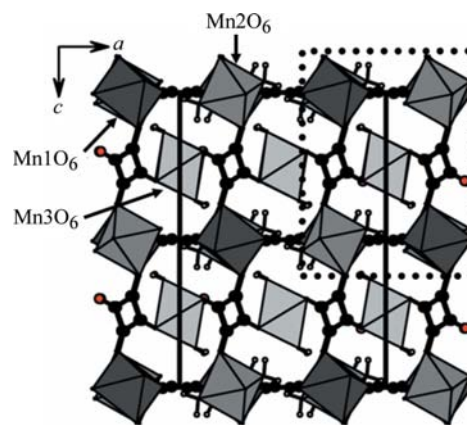

Figure 2
A polyhedral representation of the crystal structure of the title compound in the *ac* plane, showing the three-dimensional framework. The dotted lines encompass one SBU.

title compound and the cubic squarate, respectively. Thus, the smallest repeat unit is that of the trigonal structure. The multiplicity arises from the relative positions of the squarate groups within one SBU in each pseudopolymorph squarate. In the trigonal squarate polymorph, the squarate groups are eclipsed and related by lattice translations in all three directions. In the cubic squarate pseudopolymorph, the squarate groups are staggered in all three directions, leading to a doubling of all three unit-cell parameters. As an intermediate case, in the title compound, the squarate groups are staggered in the direction of the c axis and eclipsed in the two other directions, leading to the doubling of only one axis.

Alternatively, the three-dimensional coordination frameworks of the three manganese pseudopolymorph squarates can be described as cubic cages generated by the assembly of six squarate dianions, as already described for the cubic squarate (Greve & Näther, 2002).

Thermogravimetric analyses and temperature-dependent X-ray diffraction showed that the compound dehydrates in one step from room temperature until about 473 K and the anhydrous squarate decomposes to yield cubic Mn_2O_3 (see supplementary materials). After diamagnetic contribution corrections, the resulting χT versus temperature T variation suggested paramagnetic behaviour [$4.14 \times 10^{-2} < \chi_M < 1.75$ cm^3 mol^{-1}; χ and χ_M are the magnetic and molar magnetic susceptibilities, respectively]. The curve of $1/\chi$ as a function of T was fitted with a Curie law. The magnetic moment μ obtained from the straight line agrees well with the expected value for an Mn^{II} cation ($\mu_{exp} = 5.86$ μ_B, $\mu_{th} = 5.8$–5.9 μ_B; μ_B is the Bohr magneton). The interatomic distances between metallic centres are too high to allow strong magnetic interactions.

Experimental

All chemicals were of analytical grade and were used without further purification. The synthesis of the title compound was carried out by hydrothermal reaction. Equimolar amounts (3.45 mmol) of Mn^{IV}O$_2$, squaric acid and maleic acid and 3 ml of water were placed in a Teflon-lined autoclave (Paar) at 453 K for 60 h. It has been demonstrated that the addition of maleic acid is necessary to form the title compound, although its role has not been explained. The mixture was then cooled to ambient temperature at a rate of 1 K min^{-1}, leading to the formation of brown prismatic crystals, which were washed with water and dried in air.

Crystal data

[Mn$_3$(C$_4$O$_4$)$_3$(H$_2$O)$_6$]·H$_2$O
$M_r = 627.04$
Monoclinic, $C2/c$
$a = 11.5921$ (2) Å
$b = 11.8471$ (2) Å
$c = 16.5666$ (7) Å
$\beta = 90.084$ (1)°

$V = 2275.13$ (11) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.73$ mm^{-1}
$T = 293$ K
$0.19 \times 0.17 \times 0.17$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(Blessing, 1995)
$T_{min} = 0.739$, $T_{max} = 0.759$

19216 measured reflections
4984 independent reflections
3452 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.102$
$S = 1.05$
4984 reflections
172 parameters

9 restraints
Only H-atom coordinates refined
$\Delta\rho_{max} = 1.31$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—OW1	2.1465 (12)	O3—C3	1.250 (2)
Mn1—O5	2.1640 (12)	O4—C4	1.257 (2)
Mn1—O1^{ii}	2.1922 (12)	O5—C5	1.2508 (19)
Mn2—OW2	2.1456 (12)	O6—C6	1.253 (2)
Mn2—O3	2.1652 (12)	C1—C2	1.462 (2)
Mn2—O6	2.1960 (12)	C1—C4	1.466 (2)
Mn3—OW3	2.1448 (13)	C2—C3	1.464 (2)
Mn3—O2	2.1742 (12)	C3—C4	1.464 (2)
Mn3—O4	2.1831 (12)	C5—C6^{vii}	1.460 (2)
O1—C1	1.255 (2)	C5—C6	1.465 (2)
O2—C2^{viii}	1.252 (2)		
O1—C1—C2	135.89 (15)	O4—C4—C3	134.05 (15)
O1—C1—C4	134.17 (15)	C3—C4—C1	89.97 (12)
C2—C1—C4	89.94 (13)	O5—C5—C6^{vii}	136.39 (15)
O2^{vi}—C2—C1	134.07 (15)	O5—C5—C6	133.69 (16)
O2^{vi}—C2—C3	135.79 (15)	C6^{vii}—C5—C6	89.92 (13)
C1—C2—C3	90.14 (12)	O6—C6—C5^{vii}	134.07 (15)
O3—C3—C2	133.82 (15)	O6—C6—C5	135.85 (16)
O3—C3—C4	136.23 (15)	C5^{vii}—C6—C5	90.08 (13)
C2—C3—C4	89.94 (13)		

Symmetry codes: (ii) $-x, y, -z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x, -y, -z$; (viii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OW1—H1$A\cdots$O6^{vii}	0.955 (7)	1.880 (11)	2.7730 (18)	154.7 (19)
OW1—H1$B\cdots$O2^{ix}	0.953 (8)	1.833 (10)	2.7554 (19)	162 (2)
OW2—H2$A\cdots$O4^{iv}	0.946 (8)	1.872 (9)	2.7873 (18)	162 (2)
OW2—H2$B\cdots$O5^{iv}	0.947 (7)	1.861 (11)	2.7609 (18)	158 (2)
OW3—H3$A\cdots$O3^{viii}	0.959 (8)	1.850 (10)	2.7787 (19)	162 (2)
OW3—H3$B\cdots$O1	0.957 (8)	1.820 (9)	2.7505 (18)	163.2 (18)

Symmetry codes: (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (vii) $-x, -y, -z$; (viii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

The remaining maximum residual density located in the voids of the crystal structure at $(0, -0.007, \frac{3}{4})$ could be attributed to a solvent water molecule, but refinement of this position leads to large atomic displacement parameters. All H atoms were found from difference Fourier syntheses or *XHYDEX* (Orpen, 1980). They were refined with soft restraints applied on distances to their parent O atoms [0.960 (8) Å] and on H$\cdots$H distances [1.520 (8) Å] according to the geometry of the water molecule. The isotropic displacement parameters of the H atoms were fixed at $1.5U_{eq}$ of their parent O atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare et al., 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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